

CERTIFICATE OF ACCURACY

STATE OF NEW YORK)

SS:

COUNTY OF KINGS)

This is to certify that the attached document:

Patent No. JP63300576 by Applicant Mitsubishi Electric Corp.

is, to the best of my knowledge and belief, a true, complete and accurate translation
from the Japanese language into the English language.

Benardette McEvoy
Benardette McEvoy

Sworn to and subscribed before me

this 1 day of November 2005

Robert Sussman
Notary Public

ROBERT SUSSMAN
Notary Public, State Of New York
No.24-4971655
Qualified In Kings County
Commission Expires September 10, 2006

No. S63-300576

(19) Japan Patent Office (JP)

(12) UNEXAMINED PATENT GAZETTE (A)

(11) Unexamined Patent Application

No. S63-300576

(43) Published December 7, 1988

(51) Int. Cl. ⁴	ID Symbol	JPO File Number
H 01 L 31/10		D-7733-5F
G 01 J 3/02		S-8707-2G
3/50		8707-2G

Request for Examination: not yet submitted
Number of Inventions: 1 (8 pages total)

(54) Title of the Invention: Color Sensor

(21) Application No.: 62-137188

(22) Application Date: May 29, 1987

(72) Inventor: Tetsuyuki Kurata
c/o Mitsubishi Electric Corporation Materials Research Institute
8-1-1 Tsukaguchi Honmachi
Amagasaki-shi, Hyogo Prefecture

(72) Inventor: Makoto Tsunoda
c/o Mitsubishi Electric Corporation Materials Research Institute
8-1-1 Tsukaguchi Honmachi
Amagasaki-shi, Hyogo Prefecture

(72) Inventor: Yuji Hizuka
c/o Mitsubishi Electric Corporation Materials Research Institute
8-1-1 Tsukaguchi Honmachi
Amagasaki-shi, Hyogo Prefecture

(72) Inventor: Torahiko Ando
c/o Mitsubishi Electric Corporation Materials Research Institute
8-1-1 Tsukaguchi Honmachi
Amagasaki-shi, Hyogo Prefecture

(71) Applicant: Mitsubishi Electric Corporation
2-2-3 Marunouchi
Chiyoda-ku, Tokyo

(74) Representative: Ken'ichi Hayase, Patent Attorney

Continued on last page

SPECIFICATION

1. Title of the Invention
Color Sensor

2. Claim

(1) A color sensor having first and second organic colorant layers inserted between first and second conductive materials, at least one of which is light-transmitting, and a light-transmitting third conductive material inserted between said first and second organic colorant layers, characterized by

said first organic colorant layer containing at least a tetra(4-pyridyl)porphyrin skeleton and the second organic colorant layer containing at least a phthalocyanine skeleton, and

said first through third conductive materials having working functions so as to form an anisotropic junction at the side on which the light of each said organic colorant layer is incident, and an isotropic junction at the side opposite said light incident side.

3. Detailed Explanation of the Invention

[Industrial Field of Application]

This invention pertains to a color sensor. More particularly, this invention pertains to a color sensor capable of giving outputs corresponding to different light wavelengths by fabricating two photodiodes with sensitivity to different light wavelengths and subjecting the light output current of each photodiode to signal processing using an electrical circuit.

[Prior Art]

A color sensor comprising semiconductors arrayed as shown in Fig. 10 is an example of such a color sensor in prior art (Chuji Suzuki, *Electronics*, February 1982 issue, pp. 181-184).

Fig. 10 is a schematic diagram (a) and an equivalence circuit diagram (b) showing this semiconductor color sensor. This sensor has an n-type layer 55, then a p-type layer 56, formed on top of a p-type silicon substrate 54, on which three electrodes 51, 52, and 53 are disposed. First, short wavelength light is absorbed by the p-n junction in the upper part to give the photoelectric current of a photodiode PD₁ shown in (b). Next, long wavelength light is absorbed by the n-p junction in the lower part to give the photoelectric current of a photodiode PD₂. This yields two photodiode short-wavelength currents I_{1SC} and I_{2SC} for the currents shown in (b). The ratio I_{1SC}/I_{2SC} corresponds to the wavelength of the incident light. The p-type or n-type semiconductor used here is an inorganic semiconductor such as monocrystalline silicon, amorphous silicon, CdS, or PbS.

A color sensor using organic semiconductor materials has also been provided (K. Kudo and T. Moriizumi, *Applied Physics Letters*, vol. 39 (8), p. 609 (1981)). This color sensor has a zinc oxide film disposed on an ITO substrate, organic layers of merocyanine dye and rhodamine B disposed on top of this, and an aluminum electrode provided. Applying a voltage of +0.45 V to the aluminum electrode produces an electric wave flowing to the element which is proportional to the

irradiated light.

Both of the conventional color sensors discussed above, however, have drawbacks. In the first color sensor, using inorganic semiconductors for the materials produces a broad light absorption wavelength, which requires using color filters in many sensors. The inorganic semiconductors also complicate the sensor production process, and are expensive. Sensors which use organic semiconductors, by contrast, have low production costs. The second color sensor currently provided, however, has problems in terms of stable sensor operation because it requires applying a bias to the sensor and is used in the wavelength band with the least change in photovoltaic current. Furthermore, the wavelength band which the sensor can identify is from 480 nm (the peak absorption wavelength of merocyanine dye) to 580 nm (the peak absorption wavelength of rhodamine B), which is inadequate for identifying all visible light (usually 400 nm to 650 nm).

[Problems that the Invention]

The conventional color sensor configurations discussed above produce a complicated and expensive production process and other problems when using inorganic materials, or cause unstable operation and inadequate identification of all visible light when using organic materials.

This invention was developed to solve these problems. The purpose of this invention is to provide a color sensor with a simple production process, excellent operating stability, and sensitivity to a broad wavelength band encompassing all visible light.

[Means of Solving the Problems]

A color sensor according to the present invention has a first organic colorant layer containing at least a tetra(4-pyridyl)porphyrin skeleton and a second organic colorant layer containing at least a phthalocyanine skeleton inserted between first and second conductive materials, at least one of which is light transmitting, and a light-transmitting third conductive material inserted between these first and second organic colorant layers. The first through third conductive materials have working functions to form an anisotropic junction at the side on which the light of each of the organic colorant layers is incident, and an isotropic junction at the side opposite this light incident side.

[Operation]

By using two organic colorant layers containing tetra(4-pyridyl)porphyrin and phthalocyanine skeleton for the photoelectric conversion materials in this invention, the organic colorant layers have light absorption peaks on the short and long wavelength sides, and n-type and p-type semiconductor properties, which gives both layers even better efficient photoelectric conversion functions. By also skillfully combining p-type or n-type characteristics in the organic colorant layers and greater and lesser working functions in the conductive materials to form an isotropic junction at the side on which the light of each of the organic colorant layers is incident and an

isotropic junction at the side opposite this light incident side, the color sensor has improved operating stability, does not require a bias, and can fully identify all visible light wavelength bands from 450 to 600 nm.

[Working Examples]

Next, a working example of the present invention will be discussed by referring to the drawings.

Fig. 1 is a cross section of an element in a color sensor according to a working example of the present invention. In the drawing, 1 is a first conductive material, 2 is a first organic colorant layer, 3 is a third conductive material, 4 is a second organic colorant layer, and 5 is a second conductive material.

The first organic colorant layer 2 in this element contains at least a tetra(4-pyridyl)porphyrin skeleton, the second organic colorant layer 4 contains at least a phthalocyanine skeleton, and the working functions of the first and second conductive materials and 5 are greater than the working function of the third conductive material 3. If the first organic colorant layer 2 contains at least a phthalocyanine skeleton, the second organic colorant layer 4 contains at least a tetra(4-pyridyl)porphyrin skeleton and the working functions of the first and second conductive materials 1 and 5 are less than the working function of the third conductive material 3.

Specifically, the tetra(4-pyridyl)porphyrin used in the present working example is a dye with highly efficient photoelectric conversion characteristics and a light absorption peak in the short wavelength band of visible light (400 to 440 nm), and which exhibits n-type semiconductor properties (due to the effect of having a 4-pyridyl group). Examples are 5,10,15,20-tetra(4-pyridyl)porphyrin, or 5,10,15,20-tetra(4-pyridyl)porphyrin containing one metal or a mixture of metals such as Fe, Co, Ni, Zn, Cu, or Mg, either in a complex, or trapped by chemical or physical means in a polymer matrix.

Phthalocyanine is a dye with highly efficient photoelectric conversion characteristics which, in contrast to tetra(4-pyridyl)porphyrin, has a light absorption peak in the long wavelength band of visible light (550 to 700 nm) and exhibits p-type semiconductor properties. Examples are metal-free phthalocyanine, or phthalocyanine containing one metal or a mixture of metals such as Fe, Co, Ni, Zn, Cu, or Mg, either in a complex, or trapped by chemical or physical means in a polymer matrix.

These organic colorant layers are molded using conventional techniques such as casting, spin-coating, or vacuum deposition without modification.

If the first organic colorant layer 2 in Fig. 1 is a layer which contains a tetra(4-pyridyl) porphyrin skeleton, then the working functions of the first and second conductive materials 1 and 5 must be greater than the working function of the third conductive material 3, the first conductive material 1 and the third conductive material 3 must form nonisotropic junctions with the first organic colorant layer 2 and the second organic colorant layer 4, and the third conductive material and the second

conductive material 5 must form isotropic junctions with the first organic colorant layer 2 and the second organic colorant layer 4. Examples of first and second conductive materials which satisfy these conditions are metals such as Au, Cr, Pt, Ni, or Ti, or one or a combination of conductive polymers from among polyacetylenes, polypyrroles, polythiophenes, or the like which have been doped with an acceptor. Examples of third conductive materials which satisfy these conditions are metals such as Al or In, or metal oxides such as SnO_2 , ITO, or ZnO.

On the other hand, if the first organic colorant layer 2 in Fig. 1 is a layer which contains a phthalocyanine skeleton, then the working functions of the first and second conductive materials 1 and 5 must be less than the working function of the third conductive material 3, the first conductive material 1 and the third conductive material 3 must form anisotropic junctions with the first organic colorant layer 2 and the second organic colorant layer 4, and the third conductive material and the second conductive material 5 must form isotropic junctions with the first organic colorant layer 2 and the second organic colorant layer 4. Examples of first and second conductive materials which satisfy these conditions are metals such as Al or In, metal oxides such as SnO_2 , ITO, or ZnO, or one or a combination of conductive polymers from among polyacetylenes, polypyrroles, polythiophenes, or the like which have been doped with a donor. Examples of third conductive materials which satisfy these conditions are metals such as Au, Cr, Pt, Ni, or Ti.

Needless to say, the first conductive material 1 must be light transmitting if light is irradiated from the first conductive material 1 side in Fig. 1, and the second conductive material 5 must be light transmitting if light is irradiated from the second conductive material 5 side.

Next, the working principles of a color sensor according to the present working example will be discussed, taking the example of a first organic colorant layer 2 containing a tetra(4-pyridyl)porphyrin skeleton and irradiating light from the first conductive material 1 side.

The first organic colorant layer 2 is n-type, and has a peak photoelectric conversion spectrum at a wavelength λ_1 . The second organic colorant layer 4 is p-type, and has a peak photoelectric conversion spectrum at a wavelength λ_2 . The spectra of these two organic colorant layers contact at the base without overlapping. Fig. 2 shows this element.

When configuring such an element, the present element was found to comprise a serial array of organic photoelectric conversion elements provided by conventional techniques; i.e. the portion comprising the first and third conductive materials 1 and 3 and the first organic colorant layer 2 generates a negative photoelectromotive force to light of the wavelength λ_1 on the first conductive material 1 side. The portion comprising the second and third conductive materials 5 and 3 and the second organic colorant layer 4, on the

other hand, generates a positive photoelectromotive force to light of the wavelength λ_2 on the second conductive material 5 side. Although all light is irradiated from the first conductive material 1 side, incident light of the wavelength λ_2 passes through the first organic colorant layer 2 without being detected, and reaches the second organic colorant layer 4 virtually undetected. Therefore, the state of the photoelectromotive forces appearing on the first and second conductive materials 1 and 5, taking the third conductive material 3 as the reference point, for incident light varying continuously from the wavelength λ_1 to the wavelength λ_2 based on a constant light flux is as shown in Fig. 3 (where (a) is the first conductive material side and (b) is the second conductive material side).

An output with wavelength characteristics such as shown in Fig. 4 is gained by grounding the third conductive material 3 and guiding the outputs from the first conductive material 1 and the second conductive material 5 to logarithmic compression circuits, then to the (+) and (-) inputs of an operational amplifier. As a result, the wavelengths of the incident light can be specified as a range from λ_1 to λ_2 .

These working principles allow a color sensor of high sensitivity and exhibiting excellent characteristics such as reliability and stability to achieve operability using inexpensive n-type porphyrin and p-type phthalocyanine organic materials.

Moreover, the working principles discussed above are the same if the first organic colorant layer 2 contains a phthalocyanine skeleton. Only the polarities of the photoelectromotive forces outputted are reversed.

Next, specific examples will be discussed in greater detail.

Example 1

A color sensor 1 was obtained as shown in Fig. 5 by vacuum-depositing a phthalocyanine-nickel complex 14 at a thickness of about 1000 Å on top of a substrate of back glass 10 on which Cr-Au 15 had been vacuum-deposited (at respective thicknesses of 800 Å and 1000 Å), forming a SnO_2 film 13 (with about 200 Ω/\square surface resistance) by sputtering on top of this, then vacuum-depositing a zinc complex of 5,10,15,20-tetra(4-pyridyl)porphyrin 12 at a thickness of about 700 Å, and vacuum-depositing Au 11 on top of this so as to achieve about 70% transmittance (at 550 nm).

Example 2

A color sensor 2 was obtained as shown in Fig. 6 by disposing a ClO_4 -doped polypyrrole film 26 at a thickness of about 3000 Å by electrolytic polymerization on top of the substrate used in Example 1 (H. Koezuka et al., *Journal of Applied Physics*, vol. 54, p. 2511 (1983)), vacuum-depositing a metal-free phthalocyanine 24 at a thickness of about 1500 Å on top of this, vacuum-depositing Al (Al_2O_3) 23 on top of this so as to achieve about 60% transmittance (at 550 nm), then forming a chloroform solution of 5,10,15,20-tetra(4-pyridyl)porphyrin 22 at a film thickness of about 1000 Å by spin-coating, and vacuum-depositing Au 21 on top of

this so as to achieve about 70% transmittance (at 550 nm). Example 3

A color sensor 3 was obtained as shown in Fig. 7 by forming a tetrahydrofuran solution of polyvinyl chloride (PVC) and 5,10,15,20-tetra(4-pyridyl)porphyrin (30/70 ratio by weight) at a thickness of about 2000 Å by spin-coating on top of ITO substrates 10 and 35 (with about 50 Ω/\square surface resistance), vacuum-depositing Au 33 on top of this so as to achieve about 70% transmittance (at 550 nm), then vacuum-depositing a metal-free phthalocyanine 32 at a thickness of about 1000 Å, and vacuum-depositing Al 31 so as to achieve about 60% transmittance (at 550 nm).

The color sensors 1, 2, and 3 obtained in Specific Examples 1 to 3 discussed above were connected as shown in Fig. 8, then light was irradiated on all three sensors from above. A tungsten lamp was used to irradiate light through a spectrograph (Monochrometer G-250 manufactured by Nikon) to produce a wavelength band of 400 nm to 650 nm. Adjusting the gain of the logarithmic compression circuits and the operating amplifier 6 shown in Fig. 8 for each of the sensors gained strong wavelength-output voltage characteristics as shown in Fig. 9 in the range of 450 nm to 600 nm, the majority of the wavelength range of the light irradiated on the three sensors.

Change over time in the above characteristics was measured after molding the color sensors 1 to 3 in silicone resin. All of the color sensors showed hardly any change over a period of at least four months.

[Effects of the Invention]

As discussed above, this invention has a first organic colorant layer containing a tetra(4-pyridyl)porphyrin skeleton and a second organic colorant layer containing a phthalocyanine skeleton inserted between first and second conductive materials, and a light-transmitting third conductive material inserted between these first and second organic colorant layers. The first through third conductive materials also have working functions so as to form an anisotropic junction at the side on which the light of each of the organic colorant layers is incident, and to form an isotropic junction at the side opposite this light incident side. This configuration produces organic colorant layers with light absorption peaks on the short and long wavelength sides, allowing them to comprise two photoelectric conversion layers with highly efficient photoelectric conversion functions, and inexpensively produces a color sensor which does not require a bias, has excellent properties such as stability, and is capable of fully identifying all visible light wavelength bands from 450 to 600 nm.

4. Brief Explanation of the Drawings

Fig. 1 is a cross section of an element in a color sensor according to a working example of the present invention. Fig. 2 is a diagram showing the photoelectric conversion spectra of first and second organic colorant layers with peak wavelengths λ_1 and λ_2 . Fig. 3 is a diagram showing the photoelectromotive force spectra

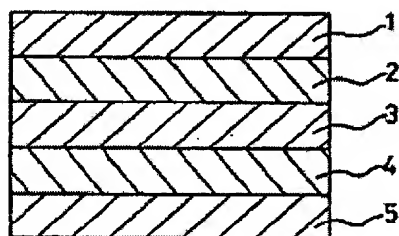
generated by these organic colorant layers. Fig. 4 is a diagram showing the output characteristics of a color sensor according to the present invention. Figs. 5, 6, and 7 are cross sections of the color sensors fabricated in Examples 1, 2, and 3 of the present invention. Fig. 8 is an element connection diagram for drawing the output of a color sensor according to a working example of the present invention. Fig. 9 is a diagram showing the wavelength-output voltage characteristics of a color sensor according to a working example of the present invention. Fig. 10 is a diagram showing a semiconductor color sensor by prior art.

1 ... first conductive material, 2 ... first organic colorant layer, 3 ... third conductive material, 4 ... second organic colorant layer, 5 ... second conductive material.

The same reference numerals in the drawings indicate the same or similar components.

Representative: Ken'ichi Hayase

Fig. 1



- 1: first conductive material
- 2: first organic colorant layer
- 3: third conductive material
- 4: second organic colorant layer
- 5: second conductive material

Fig. 2

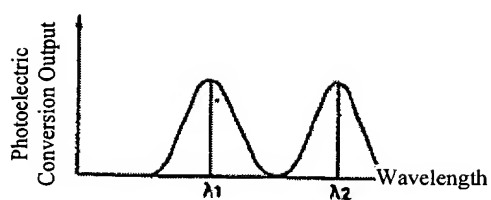


Fig. 3

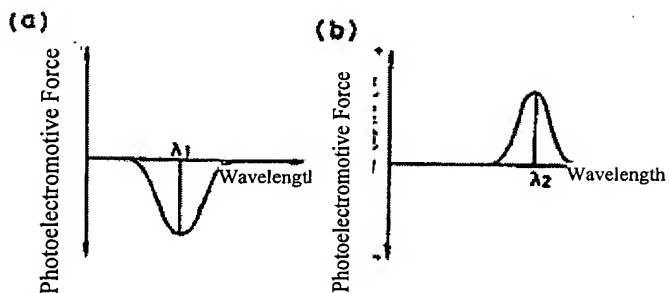


Fig. 4

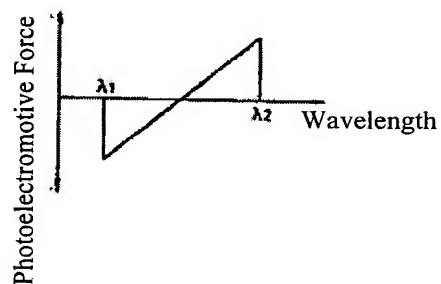
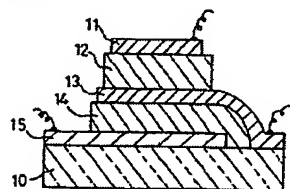
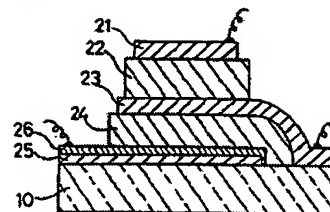


Fig. 5



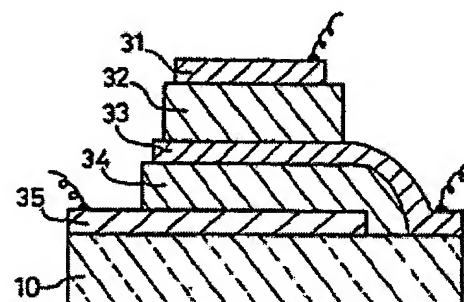
- 10: back glass
- 11: Au
- 12: 5,10,15,20-tetra(4-pyridyl)porphyrin-zinc
- 13: SnO_2
- 14: phthalocyanine
- 15: Cr-Au

Fig. 6



- 21: Au
- 22: 5,10,15,20-tetra(4-pyridyl)porphyrin
- 23: Al
- 24: phthalocyanine
- 25: Cr-Au
- 26: polypyrrole

Fig. 7



- 31: Al
- 32: metal-free phthalocyanine
- 33: Au
- 34: PVC-5,10,15,20-tetra(4-pyridyl)porphyrin
- 35: ITO

Fig. 8

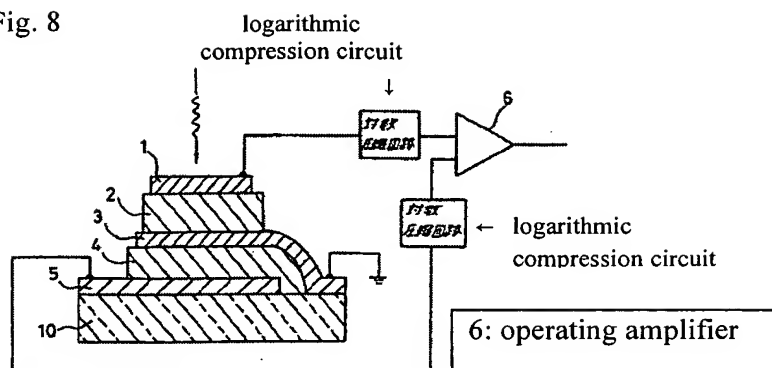


Fig. 9

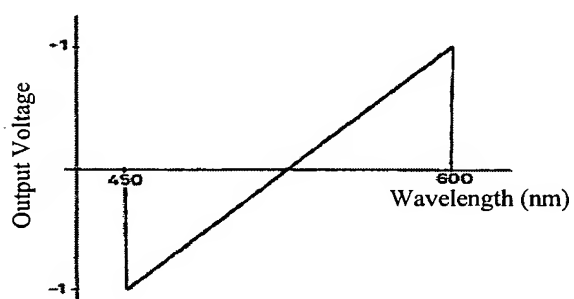
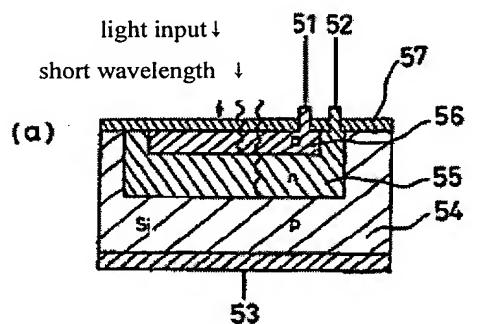
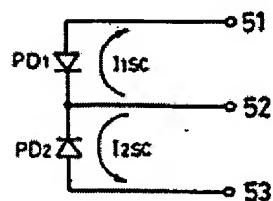


Fig. 10



51, 52, 53: electrode
57: protective film (SiO_2)

(b)



Continued from first page

(51) Int. Cl. ⁴	ID Symbol	JPO File Number
H 01 L 27/14		C-7525-5F
		K-7525-5F
31/02		A-6851-5F

(SPONTANEOUS) AMENDMENT

July 28, 1988

Hon. Director-General of the Patent Office

1. Case Identification

Japan Patent Application No. S62-137138

2. Title of the Invention

Color Sensor

3. Party Filing the Amendment

Relationship to the Case: Patent Applicant
Name: (601) Mitsubishi Electric Corporation
Address: 2-2-3 Marunouchi, Chiyoda-ku, Tokyo
Representative: Moriya Shiki

4. Representative

Name: Ken'ichi Hayase, Patent Attorney [seal]
Address: Shin Osaka Yashirodai Bldg., 4-1-45 Miyahara, Yodogawa-ku, Osaka 532
Tel: 06-391-4128

5. Part Amended

Detailed Explanation of the Invention in the Specification

6. Content of the Amendment

- (1) "Photoreducing" corrected to "photosensitive" on line 12 of page 11 of the Specification [in the original pagination; corrected in the translation].